UDC 666.642

THE USE OF NATURAL ZEOLITES FOR TILEBOARD PRODUCTION

V. M. Pogrebenkov,[1] E. D. Mel'nik,[1] V. I. Vereshchagin[1]

Translated from Steklo i Keramika, No. 1, pp. 17 – 19, January, 1998.

The possibility of obtaining ceramic facing tiles based on natural zeolite in a composition with calcium-magnesian materials (diopsidite, wollastonite, tremolite) is shown. The effect of the grinding duration on the process of thermal decomposition of natural zeolite is studied.

The construction of houses and industrial facilities requires an increase in production volume and improvement of the quality of decorative materials, in particular, ceramic tiles for interior decoration. It is important to expand the use of domestic material resources in the production of construction materials by involving in production natural resources that are currently used little or not used at all. Zeolite-containing rocks are of special interest for industry due to the abundance of these minerals (zeolite resources are estimated at over 5 billion tons) and their unique properties.

Zeolites are aqueous aluminosilicates of alkali and alkaline-earth metals having an open frame-cavity structure. The three-dimensional crystalline skeleton of zeolites is constructed of aluminosilicate-oxygen tetrahedrons [$(Si, Al)O_4$] and permeated in several directions by large cavities (pores, channels) linked with each other and with the crystal surface. The total volume of pores and channels can reach 50% of the crystal volume. The aluminosilicate frame of the zeolites is a polymeric anion whose negative charge is usually compensated on the walls of the intracrystal cavities with cations of Na, K, Ca. The intracrystal cavities and channels are made by what is known as "zeolite water" which has weak bonds with the frame and is easily released from the crystals on slow heating within the temperature range of 150 – 400°C without disturbing the frame structure. Dehydrated zeolites are capable of absorbing water again (rehydratation) [1].

At present, many deposits of natural zeolites have been investigated with the view of using them in the composition of different binding materials [2, 3]. There are few data on the application of zeolite minerals in production technology for ceramic materials, which is possibly attributable to both the variety of the zeolite minerals from different deposits and the technological peculiarities of the behavior of the zeolite, related to their structure in the composition of ceramic mixtures. Zeolite rocks are used in the compositions of ceramic tile for obtaining swollen heat-insulating materials and honeycomb catalyst cell supports [4, 5].

The present research consisted in the investigation of zeolite rocks from Sakhaptinskii deposit (Krasnoyarsk Region) represented by a genotype of volcanic-sedimentary origin. The average width of the rock is 16.2 m and the zeolite content is 43 wt.%.

In internak appearance, the rock is loose and has grains of irregular angular shape of light-brown color. The fraction is 6 ± 1 mm. The raw material is classified as clinoptilolized tuffs, tephroites.

The mineralogical composition of the zeolite rock was determined using the x-ray phase analysis and integrated thermal analysis. According to the x-ray data, the polymineral composition of the rock was found to be represented by clinoptilolite, heulandite, and mordenite in different proportions with the prevalence of clinoptilolite. The impurities are represented by quartz, albite and a small amount of argillaceous minerals.

The analysis of the behavior of the zeolites on heating (according to the data from derivatographic studies) made it possible to determine smooth continuous dehydratation, and most of the zeolite water (about 75% of the total weight loss) is removed at 400°C. The complete removal of water ends by 780°C. Three endothermic effects are observed on the differential curve: the first occurs in the range of 50 – 300°C and is determined by the removal of absorbed water, the second one in the temperature range of 450 – 580°C is related to decomposition of the argillaceous component comprising about 15% of this rock, and the third one in the interval of 800 – 870°C is associated with fracture of the crystal lattice of the rock-forming minerals. (Fig. 1)

In connection with the proposed possibility of using zeolite-containing mixtures for molding products, all testing

[1] Tomsk Polytechnical University, Tomsk, Russia.

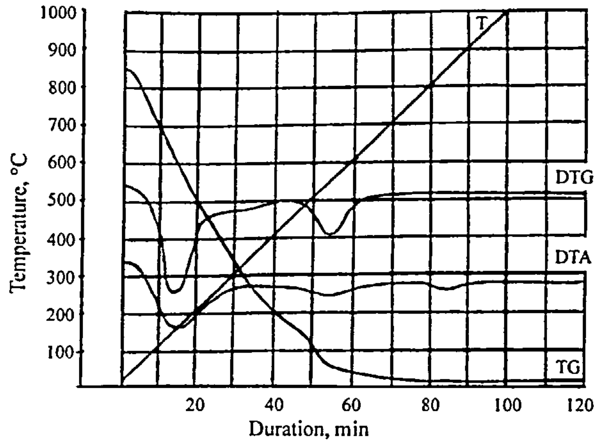

Fig. 1. Derivatogram of zeolite rock from the Sakhaptinskii deposit.

methods were used to investigate plastic properties of zeolite rocks depending on the grinding time.

Duration of grinding, h	Temperature of endothermic effects on DTA curve, °C
Initial composition	125, 531, 822
4	125, 530, 829
16	123, 519, 833
32	118, 517, 840
64	118, 519, 845
128	118, 517, 849

Zeolite rock exhibits plastic properties with an increase in the time of wet grinding in a ball mill from 4 h to 128 h, and in this case low-plasticity material (plasticity number equal to 6) is transformed into medium-plasticity material (plasticity number 16). This behavior of zeolite rock is due to amorphization of its structure and, partially, to a fuller display of the plastic properties of the argillaceous component present in the rock in an insignificant amount. The derivatograms exhibit considerable blurring of the ATA peaks and shifting of the main mass loss of zeolite water toward lower temperatures as the grinding duration increases. The second endothermic effect is shifted from 531 to 517°C due to dehydratation of the argillaceous component. Radiography exhibits a significant decrease in the intensity of the x-ray reflexes of clinoptilolite and their considerable spreading. The increase in the plasticity of zeolite rocks in the process of grinding has to be taken into account in preparation of zeolite-containing mixtures for plastic molding and semidry compaction.

It is known [4] that natural zeolite acts as a flux in the course of firing. The chemical composition of Sakhaptinskii zeolite (Table 1) also gives reason for such an assumption.

The fluxing action of the zeolites investigated was tested in a composition with clay used in the production of ceramic facing tiles. In the compositions with Voronovskii clay, the amount of zeolite varied from 10 to 50 wt.% with a 5% interval. The mixtures were prepared using the slip method with subsequent drying of slip and preparation of molding powder. Compaction was performed under a specific pressure of 20 MPa. Note the increased moisture of the molding powder (up to 13%) with a significant content of zeolite which is related to the peculiarities of the crystal structure and the increased sorption capacity of the latter. The dried samples were fired at temperatures of 1050 – 1100°C.

The data obtained confirm the assumption of the fluxing capacity of the zeolite additives introduced in clays due to an increased content of alkaline oxides in them. The introduction of 50% zeolite in Voronovskii clay results in a reduction of the sintering temperature up to water absorption below 2% from 1200 to 1050°C (Fig. 2)

The clay-zeolite compositions exhibit great firing shrinkage which ensues from the significant (up to 34 vol.%) intracrystalline structural porosity of the zeolite. In designing tile mixtures, it is necessary to obtain moderate shrinkage values. For this purpose, the minerals that proved to be successful before, i.e., wollastonite, tremolite, diopside (Table 1), were introduced into the mixtures. For the purpose of comparison, a mixture with a traditional grog (quartz sand) was tested. The composition of the mixtures tested in given in Table 2.

The mixtures were prepared by joint wet grinding of the components. The conditions of molding the samples shaped as tiles and beams were similar to those described above. Firing was carried out at temperatures of 1000, 1050, and 1100°C with a heating time at the final temperature equal to 3 min. The properties of the tiles after firing are given in Table 3.

The analysis of the data obtained shows that the effect of different grogs on sintering of clay-zeolite compositions with the same clay/zeolite ratio is not the same. The samples

TABLE 1

Component	Content, wt.%						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	R_2O	loss after calcination
Sakhaptinskii zeolite	67.56	11.75	1.98	3.90	0.70	3.57	10.56
Slyudyanskii diopside	51.43	0.20	0.08	25.40	18.60	0.73	2.16
Tuganskii sand	87.43	3.84	2.99	1.98	1.98	–	1.52
Alguiskii tremolite	39.53	0.44	0.80	26.72	15.45	–	16.36
Altai wollastonite	53.43	3.06	2.36	34.72	0.30	–	6.24
Voronovskii clay	57.84	25.63	1.66	1.15	0.94	1.37	9.81

TABLE 2

Mixture	Content, wt.%					
	Voronovskii clay	Sakhaptinskii zeolite	Tuganskii sand	Alguiskii tremolite	Altai wollastonite	Slyudyanskii diopside
1	45	40	15	–	–	–
2	45	40	–	15	–	–
3	45	30	–	25	–	–
4	45	40	–	–	15	–
5	45	30	–	–	25	–
6	45	30	–	–	–	25

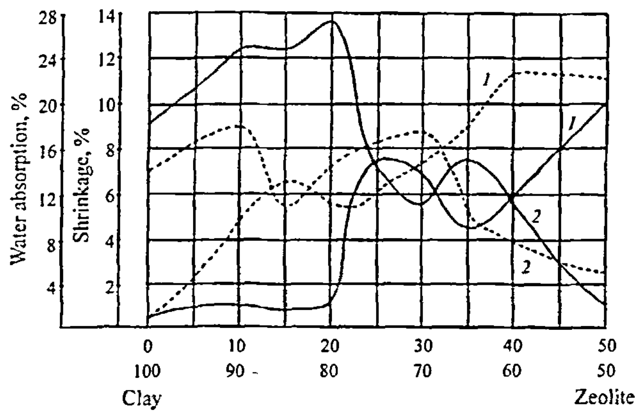

Fig. 2. Dependence of shrinkage and water absorption on the zeolite content in the mixture: 1) shrinkage; 2) water absorption; solid curves: firing temperature 1050°C; dashed curves: 1100°C.

TABLE 3

Parameter	Tiles made of mixture					
	1	2	3	4	5	6
Firing temperature 1000°C						
Shrinkage, %	1.83	1.93	1.40	1.30	1.23	2.10
Water absorption, %	24.10	26.40	25.55	23.15	25.30	19.00
Bending strength, MPa	24.00	20.60	20.80	10.70	22.60	16.90
Firing temperature 1050°C						
Shrinkage, %	3.40	2.60	1.50	1.60	1.10	3.20
Water absorption, %	21.00	24.60	26.70	22.30	24.30	17.00
Bending strength, MPa	21.20	24.60	20.70	18.30	25.60	26.10
Firing temperature 1100°C						
Shrinkage, %	8.76	9.30	4.90	4.90	8.30	7.60
Water absorption, %	9.35	8.00	17.70	13.60	8.90	8.15
Bending strength, MPa	63.80	53.70	48.30	43.10	66.30	67.60

molded from mixtures containing wollastonite and diopside were strengthened both in the stage of molding and after firing which is due to the specific habit of these minerals. The introduction of grogs makes it possible to reduce the total shrinkage of the samples but in spite of that, the water absorption after firing at 1050 and 1100°C remains substantial. This is due to both the initial structural porosity of the zeolite and the mineralogical compositions of the additives. In the case of using unconcentrated wollastonite rock, the loosening effect of the decomposing calcite impurity is exhibited, and in the case of using tremolite-calcite rock, the loosening due to decomposition of tremolite is added as well. The best additive tested is diopside.

The samples of zeolite-contenting mixtures were covered with glaze and fired in a continuous line for accelerated firing at the Tomsk ceramic plant. The glazed tiles had a satisfactory appearance except for tremolite rock compositions containing 25 wt.% wollastonite-calcite rock that revealed pricks and pimples on the glazed surface. With shrinkage of 0.7 – 2%, the water absorption of the tiles amounted to 18 – 24%.

Thus, the important possibility of using zeolite-containing rocks from Sakhaptinskii deposit in the production of decorative ceramic tiles for interior facing was established. In order to reduce shrinkage, introduction in the mixture of calcium-magnesium silicates, i.e., diopside, tremolite, wollastonite is recommended, and the content of calcite impurities in them should not exceed 10 wt.%. In introduction of zeolite rock in the composition of ceramic mixtures for producing ceramic tiles on conveyor lines, the quantity should not exceed 20 – 25 wt.% in order to reduce the shrinkage caused by the zeolite porosity.

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